SCIENCE FOR CERAMIC PRODUCTION

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IMPROVEMENT OF THE RHEOLOGICAL PROPERTIES OF CLAYEY SUSPENSIONS TREATED WITH *BACILLUS MUCILAGINOSUS* CULTURE LIQUID

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The effect of *Bacillus mucilaginosus* culture liquid on the rheological properties of clayey suspensions is investigated. It is established that the culture liquid acts as a surfactant and promotes fluidization of a clayey suspension while lowering the moisture content and increasing its sedimentation stability, which makes it possible eliminate the use of electrolytes without degrading the basic technological parameters of the slip and the properties of the intermediate product. This expands the fluidized state interval of slip, lowers the viscosity and thickening factor, and increases the rate of ceramic cast accumulation in a gypsum mold.

Key words: clayey suspensions, preparation of culture liquid, rheological properties, improvement of casting properties.

Unlike ordinary suspensions, clayey suspensions (ceramic slips) are structured systems in which the bonding between particles is due to van der Waals molecular forces and the forces between the surface charges of the particles, acting through extremely thin films of water covering the particle surfaces. Under such conditions the water films determine the structural and mechanical properties of the slip.

Water which is not bound with clayey particles and fills the volume between the particles is free and conforms to the laws of hydrostatics. The most important structural-mechanical and rheological properties of a slip can be controlled by regulating the ratio of the different types of water in a slip. The main factors of this effect are the dispersity and shape of the particles as well as the change in the viscosity, density, dielectric constant, and dipole moment of the water molecules, for which various stabilizing substances are used: electrolytes, surfactants, capillary-active substances, whose effect is to increase the water-absorbing capacity of the particles. Being absorbed on the surface of the particles, they bind a considerable amount of water, and by forming thick solvate (colloidal-adsorption, protective) shells of oriented molecules around the particles they promote separation of the particles (deflocculation) [1].

A widely used method of forming ceramic articles is casting water suspensions in porous molds. The quality of such articles is largely determined by the properties of the casting slip, the main ones being adequate fluidity with minimum moisture content, low thickening factor, good filtration properties, and resistance to separation.

The objective of the present work is to improve the rheological properties of ceramic slip based on polymineral clay, processed with *Bacillus mucilaginous* culture liquid.

The effect of a biological additive on the rheological properties was studied for a clayey suspension (moisture content 50%) consisting of low-melting clay from the Gaidukovka deposit. This clay was chosen because the “Belkhudozhkermika” JSC uses it to produce majolica articles by casting in gypsum molds.

The clay studied is characterized by polymineral composition, elevated content of free quartz (32 – 37%[3]), coloring oxides (3.42 – 5.06%), and carbonate inclusions (5 – 8%). On the basis of its mineral composition this clay belongs to the kaolinite-montmorillonite-hydromica group with the following contents (%): 23 – 29 kaolinite, 10 – 15 montmorillo-

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[3] Here and below — content by weight.

TABLE 1.

Indicator	Clayey suspension		
	initial	control	bio-treated
Thickening factor	1.19	1.18	1.06
Fluidity (30 min after standing period)	13.0	12.6	9.5
Relative viscosity, °E	2.6	2.52	1.9

nite, and 20 – 22 hydromica. This clay is classified as disperse and plastic, and it exhibits medium sensitivity to drying (according to Z. A. Nosova).

The culture liquid of *Bacillus mucilaginosus* served as a biological additive; this is a complex mixture, which includes bacterial cells of *Bacillus mucilaginosus* (strain No. 4 of the selection of the Odessa Agricultural Institute), residues of unused components of the nutrient medium, and metabolites of the bacteria (exometabolites). The cultural liquid was prepared by the following method: surface growth, from dry spore material of *Bacillus mucilaginosus* bacteria, of vegetative cells on a solid agar medium, dispersal, and deep growth of bacterial cells in a liquid synthetic nutrient medium. The metabolites of the bacteria are as follows: mono- and polysaccharides, consisting of galactose, glucose, mannose, and amino sugars; proteins; and, acid components (uronic and pyruvic acids), organic acids — volatile monocarboxylic (formic, acetic) and nonvolatile monocarboxylic (lactic, pyruvic), dicarboxylic (oxalic, oxaloacetic, succinic, tartaric), and tricarboxylic (citric) [2 – 4].

The initial clay was moistened to 50% moisture content of a water suspension containing 2 ml of culture liquid per 100 g of the dry clay matter, which constituted 300 million bacteria cells per 1 ml, and held at temperature 30 ± 2°C for 120 h. A clay suspension without bacteria (referred to below as the control) was subjected to similar isothermal maturation.

The main technological properties were determined — fluidity using the Engler method and thickening factor (see Table 1) — to study the degree of fluidization of the clayey suspensions.

The thickening factor is used to characterize the mobility of a slip poured into gypsum molds. Thickening occurs as a result of thixotropic hardening of the clay mass with reorientation of the clay particles and water molecules during long-time maturation of the slip and formation of a strong coagulation structure.

The results of the test performed on a clayey suspension subjected to bacterial treatment showed that compared with the control held under the same conditions without the introduction of bacteria the fluidity increased by a factor of 1.3 and the thickening factor decreased by a factor of 1.1.

Aggregate stability of the particles and stabilization of the slip structure are attained in the system solid phase — water-organic liquid. A decrease of the thickening factor of the slip indicates that the thixotropic reconstruction of the slip structure slows down, which could be due to the effect of the organic surfactants forming as a result of bacterial metabolism and adsorption of the substance on active sections of the clayey particles, which impedes the formation of new contacts. The improvement of fluidity and decrease of thickening factor of the clayey suspension are prerequisites for decreasing the moisture content and increasing the concentration of the dispersed phase of the suspension, which prevents comparatively large fractions of the suspension from settling. The interaction of the particles in the concentration suspension impedes their free fall and the settling rate decreases, i.e., the clayey suspension becomes more aggregation resistant.

It is known that as the dispersity of the clayey particles increases, because of the increase of their specific surface area their capacity to bind water increases and the volume of the dispersed mineral phase increases by the size of volume of the colloidal-adsorption shell surrounding a particle. Since this shell is formed as a result of the water-organic liquid phase of the suspension, the effective volume increases on account of the volume of the liquid phase. Real clay particles in the form of plates possess cavities, protuberances, and sharp edges, so that the presence of a large specific surface area in such particles changes the character of the attraction and repulsion of the particles and increases the amount of free water [1]. As a result of the presence of cavities and voids, the unbound water enters the particle and moves together with them, becoming incorporated into the effective volume of the solid mineral phase, which, most likely, should increase the viscosity. However, the relative viscosity of a bio-treated clayey suspension with optimal parameters tends to decrease. Probably, the bacterial metabolic products forming formed with adsorption on clayey particles promote, according to A. S. Michaels' schemes for the aggregation of plate-shaped particles, the aggregation of particles in a so-called "card deck," which can be compared with the quite large conditionally-spherical primary particles [1]. Such aggregates, which act as particles, are found in a deflocculated state and do not interact with one another — repulsion forces between them prevail.

It could be that aggregation of a similar kind, which decreases viscosity, occurs in slip. Therefore, the deflocculation due to colloidal-adsorption shells on the particles of the "card deck" can be explained by these shells having a resistance to shear, which keeps them from being forced out of gaps. There is no surface tension at the boundary of the colloidal-adsorption layer and free water, and such a dispersed system becomes more mobile. The electric forces developed on the surface of the particles cause the particles to repel one another.

The dependences of the combined effect of the culture liquid and electrolyte on the viscosity and thickening factor of the bio-treated and control clayey suspensions on the amount of electrolyte introduced into them are presented in

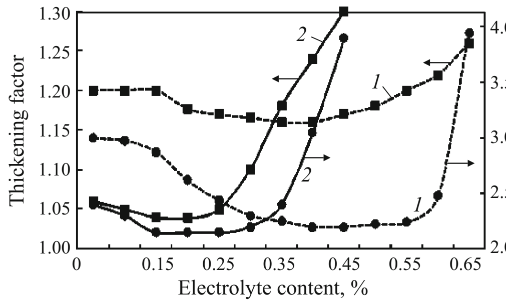

Fig. 1. Fluidization of the initial (*1*) and bio-treated (*2*) clay from the "Gaudukovka" deposit.

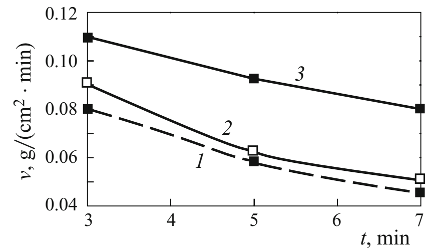

Fig. 2. Paste accumulation rate *v* versus the accumulation time *t*: *1*, *2*, *3*) initial, control, and bio-treated clayey suspensions, respectively.

Fig. 1. Soda ash was used as the electrolyte, which was introduced in the form of a solution (in steps of 0.05%) into the slips. Analysis of the data obtained showed that when 0.1% electrolyte was added to the bio-treated clayey suspension the values of the viscosity and thickening factor were considerably lower than those of the control clayey suspension and equal to 2.40°E and 1.05, respectively. The maximum fluidization, i.e., the lowest viscosity (2.2°E), with a given moisture content obtains when for the amount of soda ash introduced (0.15 – 0.35%) there is no coagulation and the content of free water is not high.

When soda ash is introduced in amounts higher than indicated above, the viscosity and thickening factor increase and a danger of coagulation arises. The maximum fluidization for the bio-treated clayey suspension is observed with the introduction of 2 times less soda ash (0.15% – 0.35%). As its content increase from 0.35 to 0.45%, the viscosity also increases. This shows that the clayey particles flocculate (stick to one another) and the suspension becomes unstable with respect to sedimentation and coagulation activity.

It was determined on the basis of previous investigations [5] that when a bio-treated clayey suspension with clay from the "Gaidukovka" deposit is filtered, 4.8% Ca^{2+} ions are transferred into the solution. When soda ash is introduced into Na_2CO_3 the Ca^{2+} ions in the sorption complex are replaced with Na^+ ions, whose concentration in the solution increases as a result of bacterial treatment. Since Na^+ ions have a greater capacity for solvation, when electrolyte is introduced the amount of loosely bound water in the diffusion layer increases, which prevents the particles from sticking to one another and increases the mobility of the system. The water of the Ca^{2+} hydrate shell transitions into a free state, and the maximum fluidization obtains. The expulsion of Ca^{2+} ions from the sorption complex of the clayey micelles is caused not only by Na^+ ions but also bacterial metabolic products. As the amount of electrolyte introduced increases, the water-organic shells coating the clayey particles become thinner, which probably results in their "house of cards" aggregation [1]. In this case free water is present in substantial amounts inside the aggregates formed and no longer fluidizes the suspension.

As a result of the combined effect of the culture liquid and electrolyte introduced in definite amounts, the concentration of the ions adsorbed on the surface of the clayey particles changes and the dissociated counterions become redistributed in the diffusion layer of the clayey micelles. The replacement of Ca^{2+} by Na^+ ions improves the electrokinetic properties. An increase of the ξ potential engenders deflocculation of the clayey suspension; this is main prerequisite for fluidization of a slip. A further increase of the number of Na^+ ions in the dispersion medium of the slip engenders compression of the double electric layer and, correspondingly, decreases the ξ potential.

Thus, it has been established that fluidization and stabilization of the clayey suspension by means of bacterial treatment are effective. As a result, slip fluidity increases substantially and the viscosity and thickening factor decrease. This makes it possible to decrease the amount of electrolyte introduced or not use an electrolyte at all.

When a water slip is poured into a gypsum (porous) mold, a casting body forms in the mold and subsequently transforms into a dense mass, which can retain the shape given it. Cast accumulation is a filtration process, to which the total resistance, slowing down the formation of a casting layer, consists of the resistances of the clayey suspension, gypsum material, and dehydrated layer (cast). The dehydrated layer contributes the highest resistance to the diffusion of moisture, since the finely dispersed, oriented particles possess low moisture conduction and are themselves hydrophyllic.

The accumulation rate of the cast depends on the formation time of the dehydrated layer, and for the experimental clayey suspensions it decreases with time (Fig. 2). It was established that the cast accumulation rate for the initial and control slips and paste accumulation time 3 min is approximately the same and equals 0.08 and 0.09 $g/(cm^2 \cdot min)$, respectively. As the accumulation time of the paste increases, the rate drops rapidly, since the cast thickening process (filtration) is damped as a result of the increase in the resistance of the dehydrated layer. When the paste of the initial and control slip is accumulated over 7 min, the cast accumulation rate equals 0.045 and 0.05 $g/(cm^2 \cdot min)$, respectively. When the clayey suspension is treated with the bioactive additive

and the optimal isothermal holding time, the cast accumulation rate likewise decreases but much less rapidly than for the control sample, equaling 0.11 g/(cm^2 · min) for 3 min and 0.08 g/(cm^2 · min) for 7 min.

Bacterial treatment of a clayey suspension increases the cast accumulation rate by a factor of 1.4, which correlates well with data obtained in a study of fluidity and thickening of the experimental suspension.

In summary, the *Bacillus mucilaginosus* culture liquid acts as a surfactant, promotes fluidization of a clayey suspension with a decrease of moisture and increases the sedimentation stability of the suspension, which makes it possible to use electrolytes without degrading the basic technological parameters of the slip and the properties of the intermediate product obtained. This permits expanding the interval of the fluidized state of slips, decreasing the viscosity from 2.6 to 1.9°E and the thickening factor from 1.19 to 1.06 and increasing the accumulation rate of the ceramic cast in a gypsum mold from 0.08 to 0.11 g/(cm^2 · min), which will make it possible to speed up the technological process of manufacturing ceramic majolica articles by the casting method.

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